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Chelating and Bridging Roles of 2-(2-Pyridyl)-benzimidazole and Bis(diphenylphosphino)acetylene in Stabilizing a Cyclic Tetranuclear Platinum(II) Complex

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Abstract

The reaction of complex [Pt(Me)(DMSO)(pbz)], **1**, (pbz = 2-(2-pyridyl)benzimidazolate) with [PtMe(Cl)(DMSO)$_2$], **B**, followed by addition of bis(diphenylphosphino)acetylene (dppac), gave the novel tetranuclear platinum complex [Pt_4Me_4(μ-dppac)$_2$(pbz)$_2Cl_2$], **2**, bearing both the pbz and dppac ligands. In this structure, the pbz ligands act as both chelating and bridging to stabilize the tetraplatinum framework. The tetranuclear Pt(II) complex was fully characterized by NMR spectroscopy, X-ray crystallography and mass spectrometry and its electronic structure was investigated and supported by DFT calculations.

Introduction

The construction of multinuclear metal assemblies has been a growing area of research during the past decade.[1] Developments based on the use of different ligands as the building unit for the synthesis of compounds have been reported for binuclear Pt complexes,[2] although to the of our knowledge, tetranuclear complexes have been rarely prepared.[3]

Wilson and Lippard reported[4] a tetranuclear platinum complex in which two acetate-bridged diplatinum(III) units are connected by two bridging amido ligands (**I**, Chart 1). The syntheses of tetranuclear platinum complexes in which the metal centers are supported by phosphido ligands have been reported by Forniés and coworkers (**II**, Chart 1).[5] Stang and Cao reported[6] the preparation and characterization, via self-assembly, of platinum- and palladium-based cationic, tetranuclear, macrocyclic complexes (**III**, Chart 1). In these complexes, 4,4′-bipyridine acts as spacer ligand between Pt centers. Youngs and his coworkers also reported[7] the synthesis of tetraplatinum square heterocycle which had large cavities and in which the rings were composed of only platinum and butadiyne fragments (**IV**, Chart 1). They used chelating phosphines in order to enforce the required *cis* geometry at the platinum atom. Yam et. al.[8] synthesized a V-shape luminescent tetranuclear platinum(II) alkynyl complex (**V**, Chart 1) and its electrochemical behavior was studied by cyclic voltammetry. Also, very recently, a tetranuclear Pt(II) compound using the 1,2,3-tetrazolate as a building block (**VI**, Chart 1) is reported[9] in which all triazolate nitrogen atoms are coordinated to 3 different Pt(II) ions. Casas and his coworker synthesized[10] a tetranuclear platinum(II)-platinum(IV) mixed-valence complexes by addition of the stoicheiometric amount of a Pt(II) reagent [*cis*-$[Pt(C_6F_5)_2(thf)_2]$ to some binuclear platinum(IV) complexes (**VII**, Chart 1).

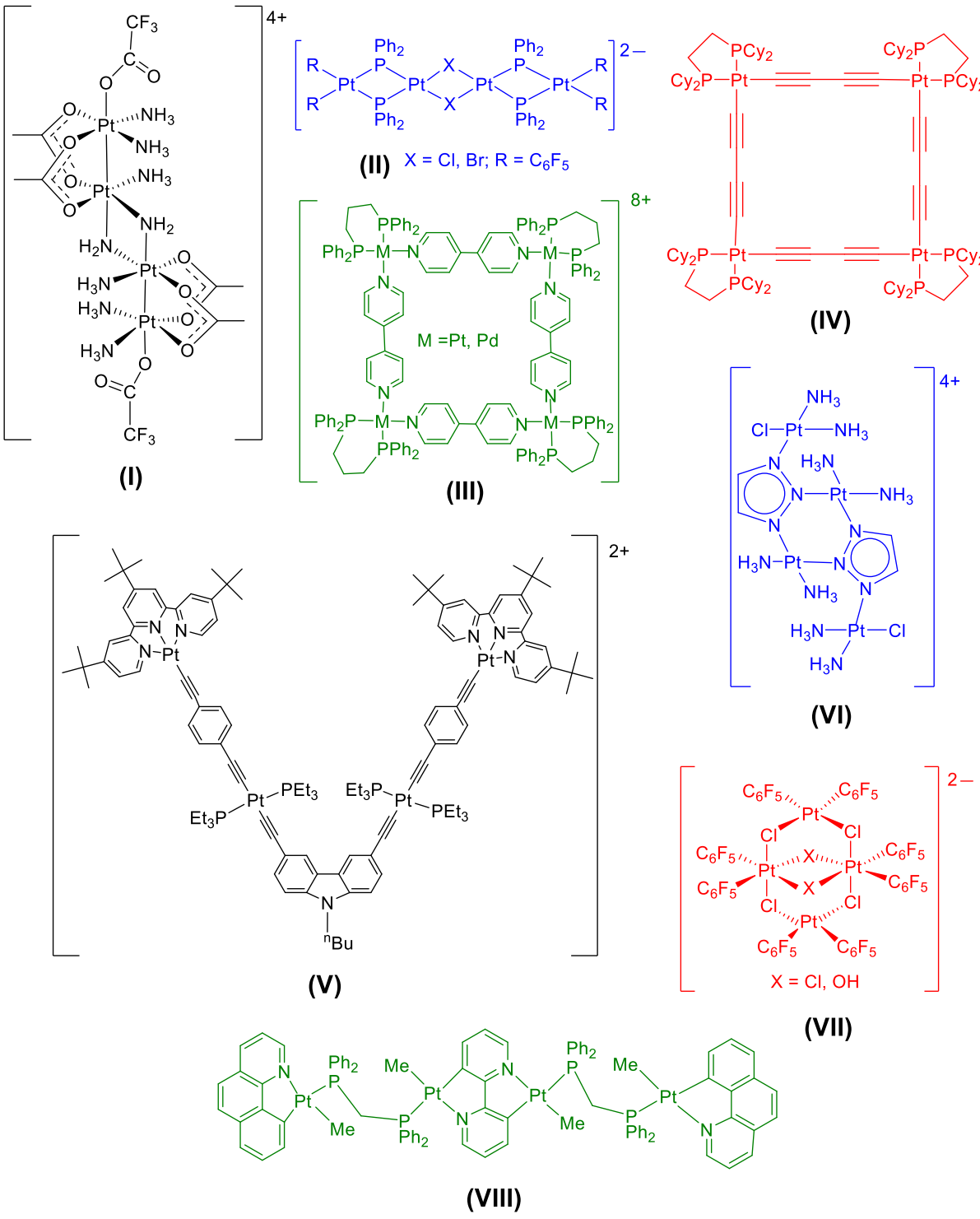


Chart 1. Examples of some tetraplatinum complexes

On the other hand, cyclometalated complexes have attracted attention because of their several applications in science.[11] Of particular interest are cycloplatinated complexes bearing strong field ligands such as benzo[h]quinolinate (bhq) and 2-phenylpyridinate (ppy).[12] The

cycloplatinated(II) compounds with the [Pt(C^N)R] moiety (C^N= cyclometalated ligand and R= alkyl, aryl or halide) are very attractive due to their ease of preparation through C-H activation of cyclometalated ligands like Hppy or Hbhq with a suitable Pt(II) precursor complex preparation.[12c-f, 13] Earlier we studied the reaction of the double rollover cycloplatinated(II) complex [Pt_2(μ-bpy-2H)$(Me)_2$(κ^1-dppm)$_2$], bpy= 2,2′-bipyridine, (in which each metallic center bears a monodentate dppm ligand) with the known monomeric cycloplatinated (II) complex [Pt(Me)(bhq)(SMe_2)] in a 1:2 molar ratio, which results in the unsymmetrical tetranuclear complex [{(bhq)(Me)Pt(μ-dppm)Pt(Me)}$_2$(μ-bpy-2H)] (**VIII**, Chart 1).[13b]

The 2-(2-pyridyl)benzimidazole (Hpbz) ligand normally acts as an anionic N^N bidentate ligand through N-H bond activation of the imidazole unit (instead of C–H activation in Hppy and Hbhq ligands).[14] Hpbz derivatives have been also used as 'bipyridine analogues' in some complexes with metal centers such as Cu(I,II),[15] Zn(II),[16] Ru(II),[17] Os(II),[18] and Re(I).[19] The ease of synthesis and the commercial availability of Hpbz are the factors that make this an attractive ligand. Although there are many reports on preparation of metal complexes in which the pbz acts as N^N bidentate ligand, the complexes bearing this ligand as a bridging ligand between two metal centers have not been explored.

Although the ability of the biphosphine ligands to form polynuclear metal complexes, in which the metal centers are supported by these bridging ligands, has produced a very rich and interesting chemistry,[13c, 20] best of our knowledge, there is no report on using 2-(2-pyridyl)-benzimidazole where it can concurrently act as a chelating and bridging ligand. These, together with our current interest in the design and synthesis of organoplatinum(II) complexes[21] have prompted us to exploit the 2-(2-pyridyl)-benzimidazole and bis(diphenylphosphino)acetylene (dppac) units as the backbone for the construction of a cyclic tetrplatinum(II) complexes. In fact, an attempt has been made to synthesize an interesting tetranuclear organoplatinum(II)

complex in which, for the first time, pbz ligands act as both chelating and bridging to stabilize the tetraplatinum framework. In this complex dppac ligands are also located as bridging ligands between Pt(II) centers. The electronic structure of this complex, supported by theoretical calculations, is also investigated.

Experimental section

General remarks

The ^{1}H and ^{31}P NMR spectra were recorded in $CDCl_3$ solutions on a Bruker Avance DPX 400 MHz spectrometer using TMS (^{1}H) and H_3PO_4 (^{31}P) as references. All chemical shifts and coupling constants are in ppm and Hz, respectively. Microanalyses were performed using a Thermo Finnigan Flash EA-1112 CHNSO rapid elemental analyzer and melting points were recorded on a Buchi 530 apparatus. UV-vis absorption spectra were recorded on a PerkinElmer Lambda 25 spectrophotometer using a cuvette with a path length of 1 cm and/or 1 mm. The complexes $[Pt(Me)_2(DMSO)_2]$, **A**,[22] and [Pt(Me)(DMSO)(pbz)], **1,**[23] were prepared by the literature method. Bis(diphenylphosphino)acetylene (dppac) and 2-(2-pyridyl) benzimidazole (Hpbz) were purchased from commercial sources.

Synthesis of Pt complexes

$[Pt(Me)Cl(DMSO)_2]$, B

This compound had been previously synthesized by the reaction of $[PtCl_2(DMSO)_2]$ with $SnMe_4$ for 24 h with a yield of 55%.[24] In an alternative method, 381 mg (1.00 mmol) of **A** and 421 mg (1.00 mmol) of $[PtCl_2(DMSO)_2]$ were added to 50 mL chloroform or acetone and stirred for 6 h. The solvent was then removed by evaporation to give 640 mg **B** (1.59 mmol). Yield: 80.0%; ^{1}H NMR in $CDCl_3$; *trans* isomer: δ 0.99 [s, $^{2}J_{PtH}$ = 78.9 Hz, 3H, Me]; 3.42, [s, $^{3}J_{PtH}$ = 24.23 Hz, 12H, Me of DMSO]; *cis* isomer: δ 1.17 [s, $^{2}J_{PtH}$ = 79.0 Hz, 3H, Me]; 3.21, [s, $^{3}J_{PtH}$ = 8.8 Hz, 6H, DMSO *trans* to Me]; 3.49 [s, $^{3}J_{PtH}$ = 38.2 Hz, 6H, DMSO *trans* to Cl].

$[Pt_4(Me)_4(\mu\text{-dppac})_2(pbz)_2Cl_2]$, 2

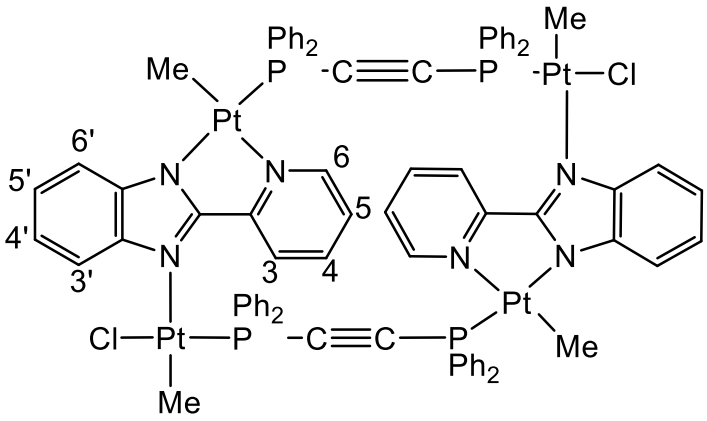


Chart 2. NMR labeling for complex **2**

$[Pt(Me)Cl(DMSO)_2]$, **B**, (401 mg, 1.00 mmol) was added to a solution of **1**, (482 mg, 1.00 mmol) in acetone (100 ml). This was stirred at room temperature for 24 h and then dppac (394 mg, 1 mmol) was added to the solution. After 20 h solvent was removed and the yellow residue was washed with cold diethylether to give 800 mg **2** (0.381 mmol). Yield: 76.0%; m.p. > 250 °C. Anal. Calc. for $C_{80}H_{68}Cl_2N_6Pt_4P_4$: C, 46.0; H, 3.2; N, 4.0 %, Found, C, 45.8; H, 3.4; N, 4.1%, NMR in $CDCl_3$: $\delta(^1H)$ 0.56 [d, $^2J_{PtH}$ = 83.5 Hz, $^3J_{PH}$ = 7.3 Hz, 6H, Me ligands *trans* to N of 2-pyridyl ring], 1.09 [d, $^2J_{PtH}$ = 72.6 Hz, $^3J_{PH}$ = 4.7 Hz, 6H, Me ligands *trans* to N of benzimidazole ring]; 8.15 [dd, $^3J_{PtH}$ = 43.6 Hz, $^3J_{HH}$ = 6.5 Hz, $^4J_{PH}$ = 5.3 Hz, 2H, H^6]; 7.84 and 7.33 [m, Ph of dppac]; 7.45 [m, $H^{6'}$ and $H^{3'}$]; 6.90 [d, $^3J_{HH}$ = 5.4 Hz, 2H, H^3]; 6.79 [t, $^3J_{HH}$ = 15.2 Hz, 2H, $H^{5'}$]; 6.58 [t, $^3J_{HH}$ = 12.7 Hz, 2H, H^5]; 6.31 [t, $^3J_{HH}$ = 15.1 Hz, 2H, $H^{4'}$]; 6.07 [d, $^3J_{(HH)}$ = 8.6 Hz, 2H, H^4]. $\delta(^{31}P)$ 27.9 [s, $^1J_{PtP}$ = 2545 Hz, 2P, *trans* to benzimidazole ring], 20.6 [s, $^1J_{PtP}$ = 4392 Hz, 2P, *trans* to Cl]. ESI-TOF-MS: m/z 2107.4 [**2** + H_3O]$^+$, 1717.4 [**2** – dppac + Na]$^+$.

Crystallographic data

Single crystal X-ray diffraction data for complex **2** were collected on a Bruker KAPPA APEX II diffractometer equipped with an APEX II CCD detector using a TRIUMPH

monochromator with a Mo Kα X-ray source (k = 0.71073 Å). The crystal was mounted on a cryoloop under Paratone-N oil and kept under nitrogen. Absorption correction of the data was carried out using the multiscan method SADABS.[25] Subsequent calculations were carried out using SHELXTL.[26] Structure determination was done using intrinsic methods. Structure solution, refinement, and creation of publication data was performed using SHELXTL. Crystallographic information is presented in Table 1. Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, No. CCDC 1874226. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44(1223)336-033, e-mail: deposit@ccdc.cam.ac.uk, or www.ccdc.cam.ac.uk.

Table 1. Crystal and structure refinement for complex **2**.4$(CH_3)_2CO$.

Empirical formula	$C_{92}H_{92}Cl_2N_6O_4P_4Pt_4$
Formula weight	2320.85
Temperature (K)	100(2)
Wavelength(Å)	0.71073
Crystal system	Triclinic
Space group	P-1
a/Å	11.207(3)
b/Å	11.658(3)
c/Å	17.085(5)
ß/°	94.774(7)
VolumeÅ^3	2151.6(10)
Z	1
Density (calculated)/ Mg/m^3	1.791
Absorption coefficient/mm^{-1}	6.672
F(000)	1124
Theta range for data collection	1.229 to 27.266°
Reflections collected	18876
Independent reflections, [R(int)]	9565, [0.0356]
Max. and min. transmission	0.7455 and 0.5607
Data / restraints / parameters	9565 / 0 / 511
Goodness-of-fit on F^2	0.976
R1/wR2 [I>2sigma(I)]	0.0294/ 0.0596

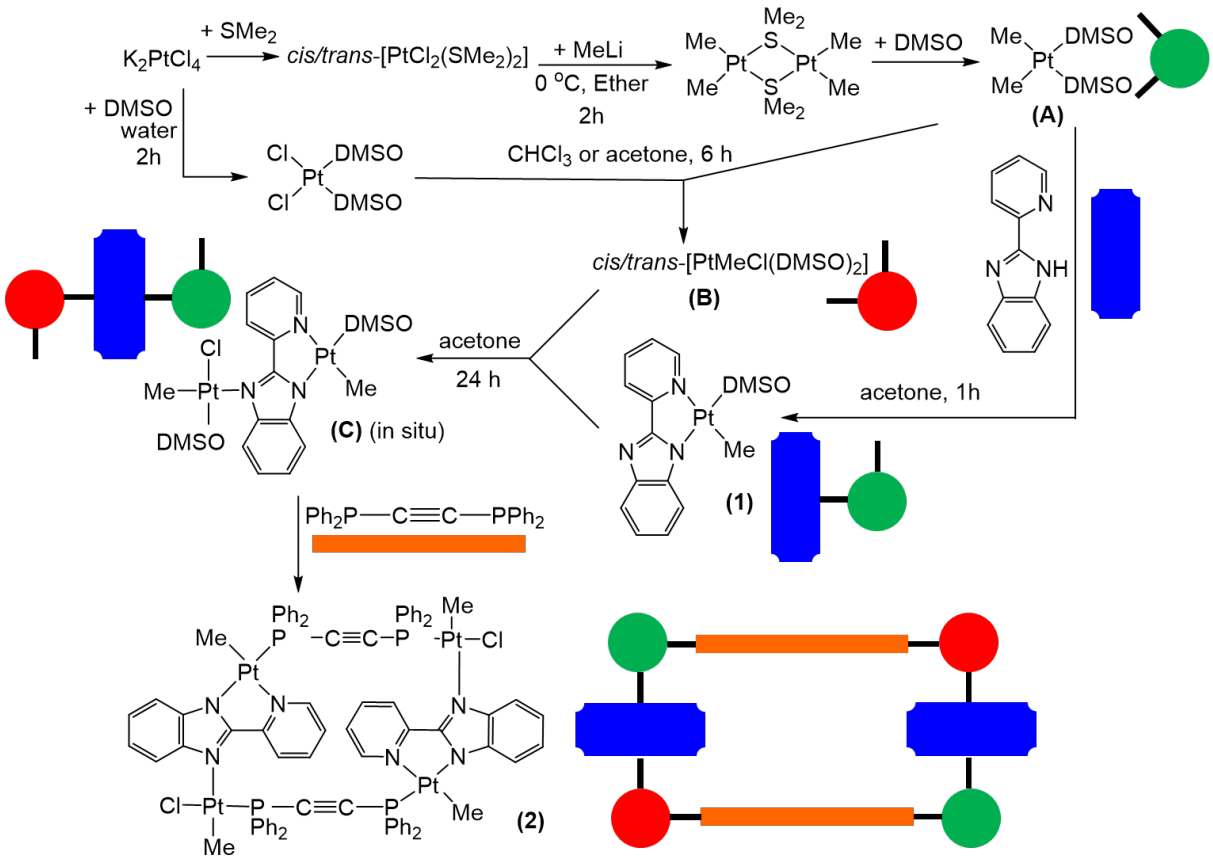
Computational details

Gaussian 09 was used[27] to fully optimize the structure at the B3LYP level of density functional theory. The effective core potential of Hay and Wadt with a double-ξ valence basis set (LANL2DZ) was chosen to describe Pt.[28] The 6-31G(d) basis set was used for all other atoms. To evaluate and ensure the optimized structures of the molecules, frequency calculations were carried out using analytical second derivatives. In all cases only real frequencies were obtained for the optimized structures. The calculations for the electronic absorption spectra by time-dependent DFT (TD-DFT) were performed at the same level of theory. The compositions of molecular orbitals and theoretical absorption spectra were plotted using the "Chemissian" software.[29]

Results and Discussion

Complex synthesis and characterization

The detailed synthetic route for the tetranuclear complex $[Pt_4(Me)_4(\mu\text{-dppac})_2(pbz)_2Cl_2]$, **2**, is depicted in Scheme 1. The precursor complex [Pt(Me)(DMSO)(pbz)], **1**, was prepared through the reaction of $[Pt(Me)_2(DMSO)_2]$, **A**, with Hpbz in 1:1 ratio. In the key step complex **B** was added to a solution of **1** in acetone to produce an intermediate which is suggested to be the dimeric Pt complex [Cl(Me)(DMSO)Pt(μ-pbz)Pt(Me)(DMSO)], **C**. Then, dppac was added in situ to the solution to result in the assembly of **2** as a yellow solid.



Scheme 1. Route to preparation of complex **2**

The structure of the new complex **2** was fully characterized using multinuclear NMR spectroscopy (^{1}H and ^{31}P{^{1}H} NMR), electrospray ionization mass spectroscopy (ESI-MS) and X-ray crystallography. The ^{31}P{^{1}H} NMR spectrum is illustrated in Fig. 1A (details of the numerical NMR data are collected in the Experimental section). The ^{31}P{^{1}H} NMR spectrum of **2** displays two distinct singlets with equal intensities, having platinum satellites. They appear at δ = 20.6 ($^{1}J_{PtP}$ = 4392 Hz) and 27.9 ($^{1}J_{PtP}$ = 2545 Hz), which are respectively assigned to the P *trans* to Cl and the P *trans* to ligating N atom of benzimidazole ring, in agreement with high *trans* influence of N compared to Cl. It should be noted that the $^{1}J_{PtP}$ values of 4264 and 3081 Hz were previously reported for P atom *trans* to Cl in complexes [Pt(Me)(dppe)Cl] (dppe = $Ph_2PCH_2CH_2PPh_2$) and [$PtCl_2$(dppm)] (dppm = $Ph_2PCH_2PPh_2$),[30] respectively. On the basis of the ^{1}H NMR spectrum of **2** (see Fig. 1B), two different Me groups are observed, being *trans* to

pyridyl and benzimidazole rings. The Me group *trans* to ligating N of pyridyl was observed to be appeared at δ = 0.56 as a doublet signal with $^{2}J_{PtH}$ = 83.5 Hz and $^{3}J_{PH}$ = 7.3 Hz. Whilst, the Me group *trans* to ligating N of benzimidazole ring was appeared at δ = 1.09 ppm with a considerably lower $^{2}J_{PtH}$ = 72.6 Hz and $^{3}J_{PH}$ = 4.7 Hz values. It indicates more *trans* influence of ligating N of benzimidazole ring in comparison to that for 2-pyridyl ring.

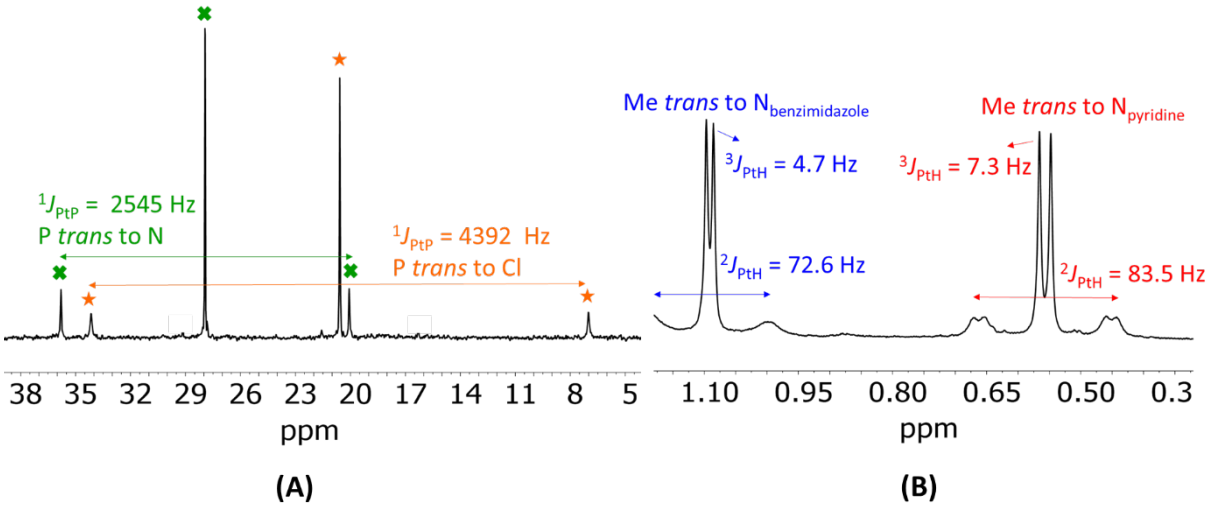


Fig. 1 (A) ^{31}P and (B) ^{1}H (aliphatic region) NMR spectra of the complex **2**.

Crystal Structure

Yellow crystals of complex **2** were obtained upon diffusion of *n*-hexane vapor into the acetone solution. The structure obtained by X-ray crystallography technique is presented in Fig. 2 and the numerical data are summarized in Table 1 (see the caption of Fig. 2 for selected geometrical parameters). To the best of our knowledge, the complex **2** is the first example of a tetranuclear Pt complex having both bridging 2-(2′-pyridyl)-benzimidazolate and bis(diphenylphosphino)acetylene ligands. In this structure, pbz ligands act as both chelating and bridging ligand to stabilize the tetraplatinum framework. The molecular structure of complex **2** certifies that the $Pt_4(dppac)_2(pbz)_2$ framework was formed. As shown in Fig. 2, the solid state structure exhibits distorted four-coordinated square planar geometry around the platinum centers. The methyl groups are *trans* to the pyridyl and benzizmidazole rings of pbz

ligand. The largest deviation from ideal square planar geometry belongs to the N3-Pt2-N2 angle at 78.01(13)° which is associated with the Pt(pbz) chelate ring. One of P atoms of dppac ligand is located *trans* to ligating N of benzimidazole ring (Pt2-P2 = 2.1910(13) Å) and another one is *trans* to Cl atom (Pt1-P1 = 2.1754(12) Å). The Me groups are located *trans* to the ligating N of the pyridyl (Pt2-C26 = 2.054(4) Å) and benzimidazole (Pt1-N1 = 2.122(3) Å) rings (See Fig. 2). Therefore the structure of complex **2** confirms that "Pt(μ-pbz)Pt" moieties are connected through dppac bridging ligand in which the P-C-C-P fragment is almost linear. The terminal Me ligands are *transoid* in relation to each other. It should be noted that this kind of bridged dppac complexes where a dppac molecule acts as a bridging ligand between two metal fragments are not common.[2a, 30-31]

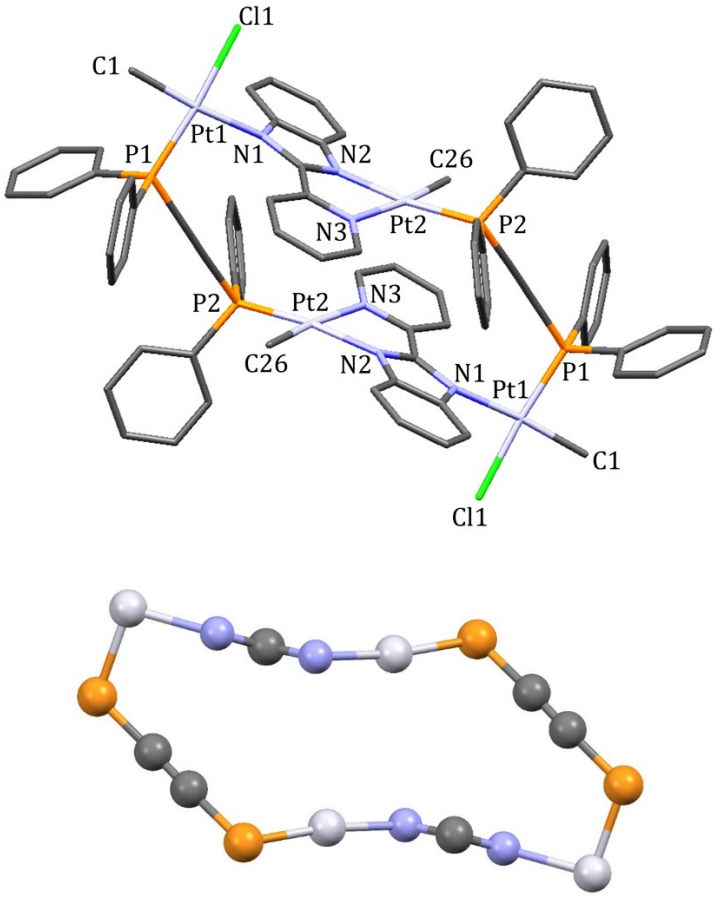


Fig. 2 (Top) Structure of complex **2**. All hydrogen atoms and solvent molecules are omitted for clarity. Selected geometrical parameters (Å, deg.): Pt1-Cl1 2.3597(12); Pt1-C1 2.064(4);

Pt1-P1 2.1754(12); Pt1-N1 2.122(3); Pt2-N2 2.078(4); Pt2-N3 2.134(3); Pt2-P2 2.1910(13); Pt2-C26 2.054(4); Cl1-Pt1-N1 88.28(10); Cl1-Pt1-P1 175.11(4); Cl1-Pt1-C1 86.89(12); N1-Pt1-P1 96.52(10); P2-Pt2-N3 104.73(10); P2-Pt2-C26 83.69(13); N3-Pt2-N2 78.01(13); N2-Pt2-C26 93.63(16). (Bottom) 18-membered $Pt_4P_4N_4C_6$ central core of tetranuclear complex **2**.

ESI-MS result further confirms the molecular formulae formation by demonstrated isotopically well-resolved peak at *m/z* = 2107.4 which is related to [**2**+H_3O]$^+$. The peak matched well with its calculated theoretical isotope distributions (see Fig. 3).

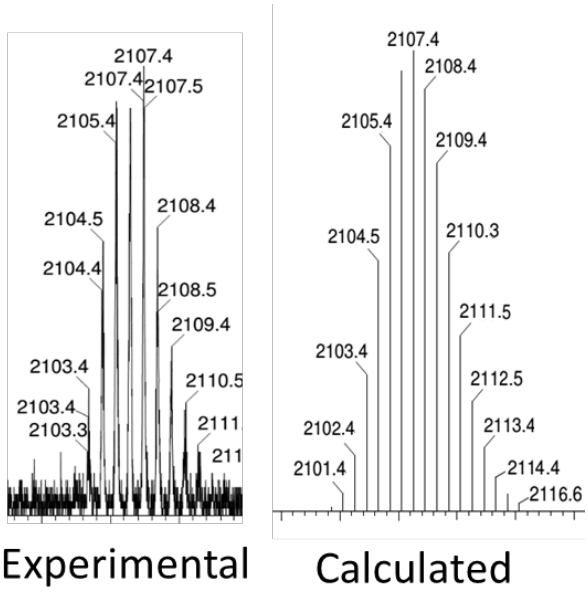


Fig. 3 Expanded (left) and simulated (right) isotopic pattern ESI-MS spectrum of complex [**2**+H_3O]$^+$, showing the expected intensity due to isotopic distribution.

Absorption spectrum

Complex **2** is stable in most of common organic solvents including acetone, CH_2Cl_2, $CHCl_3$ and CH_3CN which allows the investigation of its absorption spectrum in a wide range of solvents. Fig. 4A shows the absorption spectrum of **2** in different solvents; the numerical data are listed in Table 2. The complex **2** shows intense absorption bands in the 300-400 nm

region I all solvents. As an example, two absorption bands at 312 and 358 nm ($\varepsilon = 3.00\times10^4$ and 2.60×10^4 M^{-1} cm^{-1}, respectively) appear in CH_2Cl_2 solvent. In order to gain further insight into the nature of electronic transitions for the complex **2** in CH_2Cl_2, TD-DFT calculations were performed on the optimized ground state geometries. As shown in Fig. 4B, the computed absorption wavelengths (bars) are in good agreement with its experimental spectrum. The numerical data for the selected calculated wavelengths together with their assignments are listed in Table 2. For the complex **2**, the plots of molecular orbitals, the energies of the selected molecular orbitals together with their compositions in terms of ligands and metals are shown in Fig 5. The absorption bands at higher energies are attributed to L′LCT, IL and MLCT (L=pbz and L′= Cl).

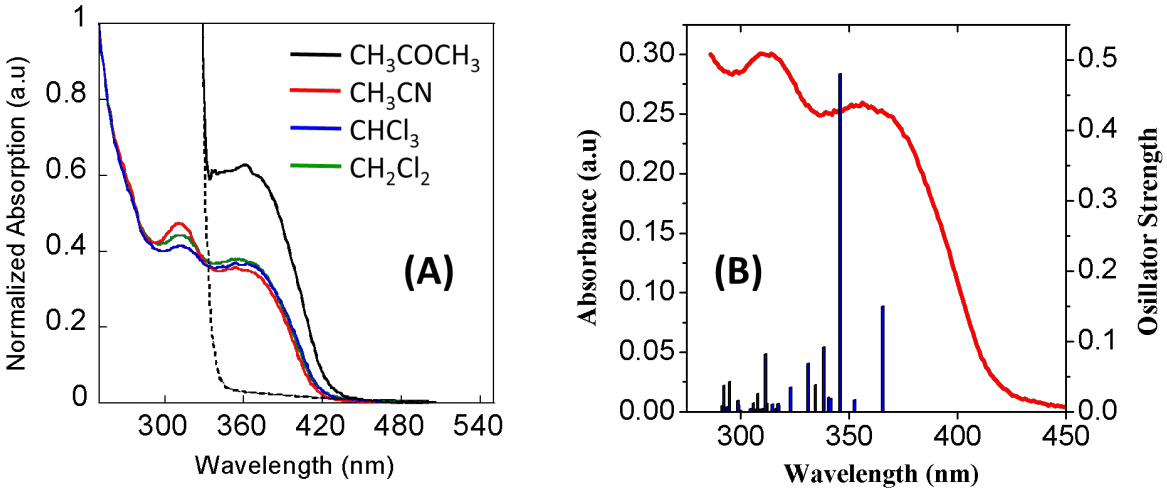


Fig. 4 (A) UV-visible absorption spectrum of complex **2** at different solvents (1.0×10^{-5} M); dash line shows the UV-visible spectrum of acetone, UV cutoff of acetone is 330 nm. (B) Overlaid experimental absorbance (spectrum) and calculated TD-DFT (bar) for the complex **2** in CH_2Cl_2.

Table 2. TD-DFT computed spectra and experimental wavelength (nm) for the complex **2** (1.0×10^{-5} M) at the ground state geometry in CH_2Cl_2 solution (only transitions with a probability higher than 20% are reported).

λ_{cal} (*f*)	λ_{max}(exp)	Transitions (probability)	Assignments
			(L=pbz, L′= Cl, L″ = dppac)
345 (0.480)	312	HOMO-3 – LUMO+1 (46)	L′LCT, MLCT, IL
		HOMO-2 – LUMO (35)	IL, L′LCT, MLCT
365 (0.150)	358	HOMO – LUMO (63)	L′LCT, MLCT
		HOMO-1 – LUMO+1 (29)	L′LCT, MLCT

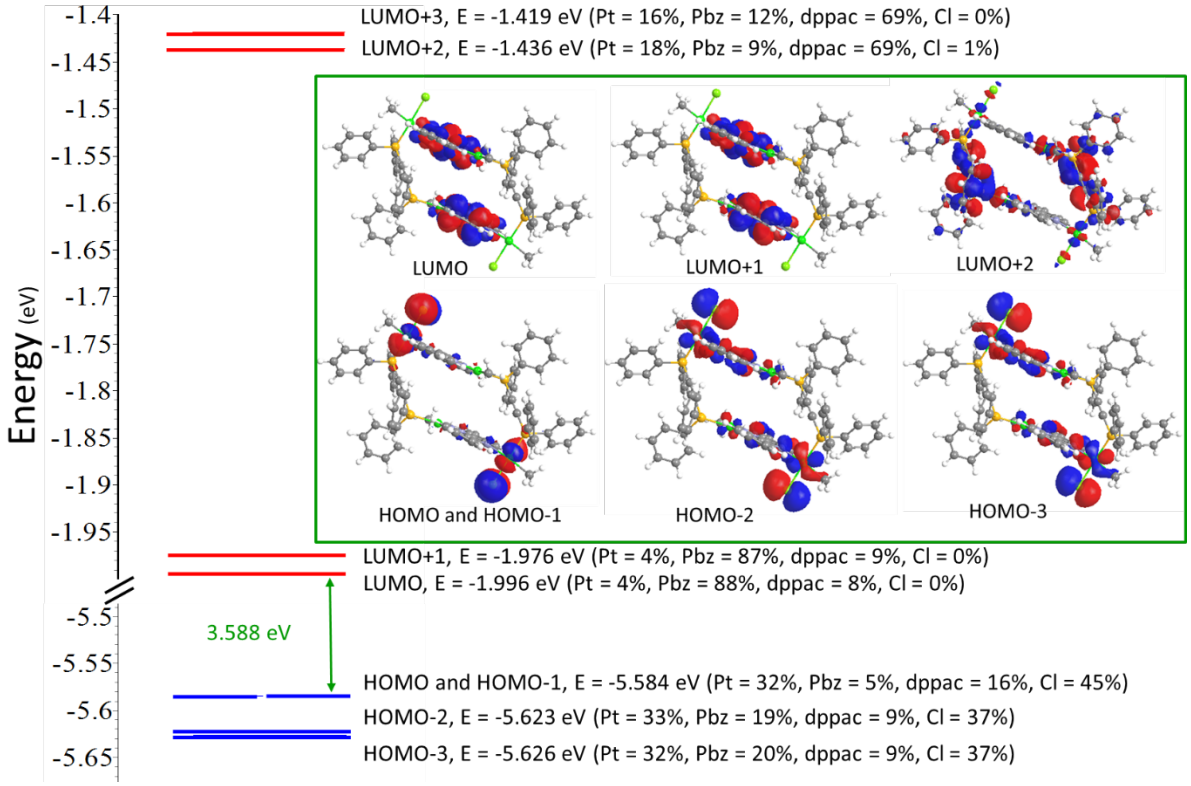


Fig. 5 Representative frontier orbitals and the relative composition energy levels for complex **2**.

The partial molecular orbital diagram for the tetranuclear platinum complex **2** with the several highest occupied and lowest unoccupied molecular orbital contours are depicted in Fig. 5 and the distribution of important frontier orbitals in the ground state and the corresponding partial

molecular orbital composition (percentages) are provided. The values of the HOMO–LUMO energy gap is equal to 3.588 ev. Analysis of the frontier molecular orbitals reveals that the maximum contribution in HOMO and HOMO-1 (the highest occupied molecular orbital) belongs to the Cl ligand and Pt metal center (in PtMeClNP moity) with small contribution of dppac ligand. In addition, the results show that LUMO and LUMO+1 (lowest unoccupied molecular orbitals) are significantly localized on pbz bridging ligand, and LUMO+2 is contributed on dppac ligand.

Conclusions

Reaction of complex [Pt(Me)(DMSO)(pbz)], in which pbz = 2-(2-pyridyl)benzimidazolate, with [Pt(Me)Cl(DMSO)$_2$] in the presence of bis(diphenylphosphino)acetylene (= dppac) leads to a rare tetranuclear Pt(II) complex in which two 2-(2-pyridyl)-benzimidazolate ligands act as both chelating and bridging ligands to stabilize the tetraplatinum(II) complex. Dppac ligands are coordinated between Pt centers in a bridging mode *via* P-donor atoms, making a cyclic tetranuclear platinum complex. Investigation of electronic structure and related DFT and TD-DFT calculations supported a mixed MLCT (metal-to-ligand charge transfer) and L′LCT (ligand-to-ligand charge transfer) and IL (Intra ligand) transition (L=pbz, and L′= Cl).

ASSOCIATED CONTENT

Supporting Information

The computational details for complex **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interests.

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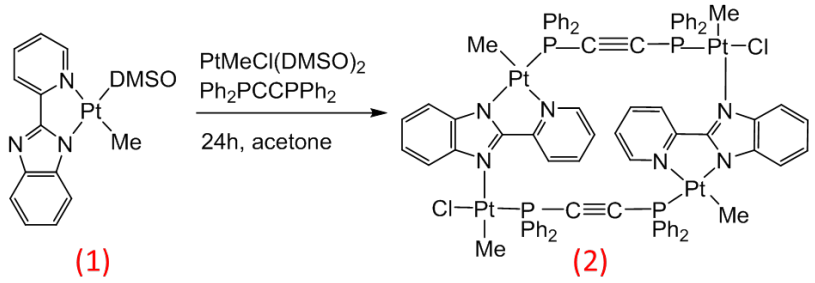
SYNOPSIS TOC

An interesting cyclic tetranuclear Pt(II) complex, **2**, is synthesized by the reaction of **1** with [PtMe(Cl)(DMSO)2], followed by addition of dppac, bearing both the pbz (= 2-(2-pyridyl)benzimidazolate) and the dppac (= bis(diphenylphosphino)acetylene) ligands. The complex is the first example in which the pbz ligands act as both chelating and bridging to stabilize the tetraplatinum framework.



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